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Determining the Surface and Interface Structure of Nanomaterials

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Abstract

This paper informally speculates on the challenges of determining the atomic-scale surface and interface structure of nanomaterials. The relative capabilities of different techniques are compared. This includes discussion of theoretical methods needed to interpret experimental techniques.

Low-dimensional structures

Nanoscience and nanotechnology today already include materials with a very wide variety of shapes and combinations of dimensions. Among the many shapes of nanostructures we may list: quantum dots, nanoparticles, nanorods, tetrapods, nanowires, ultrathin films, wedges, multilayers, and nanograins or nanodomains.

An essential feature of such nanostructures is that at least one dimension must have a nanometer scale. Surfaces and interfaces are crucial components of nanostructures, thereby establishing a bridge to more traditional surface science. Even the "bulk" of nanomaterials can deviate structurally from the bulk of the corresponding infinitely-extended material, due to the proximity of interfaces.

However, in nanoscience and nanotechnology, the solid-vacuum interface (the traditional surface of surface science) is the exception rather than the rule: instead, solid-solid, solid-liquid, solid-gas, liquid-liquid and liquid-gas interfaces will form the great majority. The structure of these interfaces is largely unknown at present. Furthermore, "soft matter", meaning primarily biomaterials, also will play a very large role, giving rise to solid-soft, soft-liquid and soft-gas interfaces that have received even less attention in surface science, particularly with structure determination.

With such a wide variety of shapes and dimensions, it becomes clear that the challenge of determining the atomic-scale nanostructure will require many different approaches. There is also a great need for new methods to determine such structure.

It is desirable to obtain structural information both on the atomic scale and on the nanoscale, or even on the mesoscale. Structure both parallel to and perpendicular to interfaces can be important. On the atomic scale we need bond lengths, bond angles, and crystallographic data when the material is at least partly crystalline. On the nanoscale, it is desirable to characterize the three-dimensional shapes and orientations of grains, domains, nanoparticles, quantum dots, etc.

Surface science has solved a good number of surface structures since its modern development in the 1970s: according to the Surface Structure Database [1], this number is currently around 700 distinct detailed structures. Most of these are solid-vacuum interfaces; less than 10 are solid-solid interfaces; no other kinds of interfaces are known in enough detail to be represented in this database. We may ask whether this is sufficient to do nanoscience and nanotechnology. To put this number in perspective, let's compare it with corresponding numbers of known structures in other fields.

Structural databases of proteins include roughly 10,000 solved structures, an order of magnitude more than we have for surfaces and interfaces. Molecular structures number roughly 100,000, another order of magnitude more. And inorganic databases also total something like 100,000 structures. These structures of proteins, molecules and inorganic materials form the basis of much of modern biology, chemistry, materials science and physics, not to speak of all the related technologies.

We can make a very rough guess at the number of interfaces that might be relevant to nanoscience and nanotechnology. The crucial difference compared to molecules, inorganics, etc., is that we are now speaking of two or more materials interfaced to each other, with possibly other materials sandwiched between them, thus greatly multiplying the number of possible structures. First, let's assume that there are 100 elements in the Periodic Table: then there are ~ 100 x 100 = 10,000 possible interfaces between two elementally pure materials; this should be multiplied by the number of relevant crystallographic faces for each material, conservatively 3 for each, giving a total around 3 x 3 x 10,000 ~ 100,000 interface structures. If we allow compounds, as well as sandwiched foreign matter, the number of distinct interfaces is further multiplied by orders of magnitude. The result vastly exceeds even the number of molecules and inorganic materials for which we know the atomic-scale structure.

I conclude that the 700 or so currently known surface structures don't begin to "scratch the surface" of nanostructure knowledge, especially considering that they are almost all solid-vacuum structures! Unfortunately, there is a universal tendency at present to try to ignore atomic-scale structure in nanoscience: this attitude cannot continue without turning nanoscience into an empirical science with much less impact. As one analogy, try to imagine how semiconductor and computer technology would have evolved without knowledge of the structure of silicon and its resulting band structure.

Techniques for surface and interface structure determination

Surface science has evolved a large number of techniques that provide structural information about solid-vacuum surfaces and, to a lesser extent, other interfaces. I shall briefly list here several prominent techniques, without claim of completeness or balance.

Photon-in/photon-out techniques

The techniques that only use photons as the incident and detected probes have a major advantage over those using electrons: they do not require vacuum, and thus are well suited to study "buried" interfaces, distant from the nearest vacuum, common in nanostructures. On the other hand, these methods are inherently less sensitive to surfaces and interfaces, so that special measures must be taken to probe interfaces rather than bulk material. These techniques include the following: x-ray diffraction (XRD), in particular micro x-ray diffraction; x-ray absorption fine structure (XAFS) and x-ray emission spectroscopy (XES); Fourier transform infrared spectromicroscopy; x-ray holography and tomography.

Particle-based techniques

The main particles used to study surface and interface structures are electrons and ions (such as He and alkali ions). Their strong interaction with matter gives them a short mean free path that has been exploited to study the solid-vacuum interface. Solid-gas interfaces can be sampled with some difficulty, using appropriate geometries to limit the path of the charged particles through the gas.

To study buried interfaces requires special approaches (such as shallow burial near vacuum, or deep channeling of ions). Examples of such techniques include: photoelectron diffraction (PED) and inverse photoelectron spectroscopy (IPES); low-energy electron diffraction (LEED); ion scattering spectroscopy (ISS); a variety of microscopies, such as transmission electron microscopy (TEM), photoemission microscopy (PEEM) and low-energy electron microscopy (LEEM); convergent-beam LEED (CBLEED); scanning tunneling microscopy (STM); electron holography and tomography.

Theory

Thanks to increasing computer performance and improving theoretical methodologies, theory plays an ever-increasing role in understanding atomic-scale and nanoscale structure. In view of the increasing challenges for experimental determination of surface structure, it is very likely that theory will continue to grow in relative importance. A major role for theory will be predictive and exploratory studies: in many cases, it will be far easier to try out new materials and geometries computationally rather than experimentally.

Nonetheless, theory will continue to involve compromises between achievable complexity and accuracy, due to the computational cost and the insatiable desire to model ever-greater complexity. As a result, approximations will always have to be made, and these will need verification on (relatively simple) model systems by comparison with both better theoretical methods and experiment.

A special function of theory is to enable the interpretation of experiment, in particular diffraction (XRD, LEED, PED): such "theory of the experiment" is central to determining atomic-scale structure by modeling the experiment so as to extract the structural quantities of interest (bond lengths, bond angles, etc.).

Theory will also play a major role in interpreting STM images, due to the complexity of the imaging process, which depends not only on the structure of the sample and of the imaging tip, but also on the electronic structure of both sample and tip surface, as well as on the tunneling geometry and energetics. At present, very few STM images are being interpreted by theory, dramatically raising the risk of misinterpreting bumps as atoms and dips as vacancies, for example. Since STM promises to remain a central tool for studying nanostructures, the value of theory for interpreting its images will most likely increase.

Spatial resolution in microscopies

Direct imaging of nanostructures is very valuable and already much practiced, especially with TEM: however, we may ask whether atomic resolution is attainable. Here I sketch the current state of microscopic resolution of various relevant microscopies. In this regard, it must be remembered that it is difficult to get directly comparable numbers for resolution, since this quantity depends on many factors, including date of reporting: so our numbers should only be viewed as rough guidelines.

Photons only

The resolution of microscopies that use only photons is usually limited to the wavelength or the skin depth (mean free path). This applies, for instance, to x-ray microscopy (XRM) and scanning near-field optical microscopy (SNOM): while these techniques may, in some cases, offer chemical distinction, they are structurally limited ultimately by wavelength or skin depth to ~10 nm, in practice more like ~20-30 nm.

Electrons only

With most microscopies that use electrons, the resolution is limited primarily by the electron optics. The resulting resolution can reach better than ~0.1 nm in TEM (when imaging columns of atoms), but more typically ranges from ~8 to ~25 nm. With STM, a resolution of ~0.2 nm is common (although strictly speaking only in two dimensions, excluding the dimension perpendicular to the surface, for which theory is needed).

Combined photons and electrons

For those microscopies that combine the use of photons and electrons, the resolution is limited by either the electromagnetic optics or the electron optics to ~15-50 nm. This applies in particular to PEEM, including x-ray PEEM, and PED performed in LEEM.

Three-dimensional microscopy: holography

The principle of holography is the reconstruction of a 3D image from 2D diffraction patterns, which are then called holograms for the occasion.

In the case of x-ray holography and high-energy electron holography, an external electron source is used. The resolution is then typically limited by the optics to ~10-30 nm; if, however, the holographic transform from hologram to 3D image is performed computationally (essentially by a Fourier transformation), then the resolution is limited by the atomic scattering properties such as phase shifts to ~0.1 nm.

With low-energy electron holography (using photoelectrons or LEED electrons), the method uses internal point sources and the holographic reconstruction is computed: the resolution is then primarily limited by atomic scattering properties to ~0.1 nm.

Three-dimensional microscopy: tomography

Tomography reconstructs a 3D image from multiple transmission images, by a computational approach. The present resolution using electrons is ~30 nm.

In the more or less distant future, electron tomography may be able to produce 3D atomic resolution for individual atoms. Such an achievement would be a unique breakthrough, as other techniques image not a single atom, but an average over many identical atoms (STM does image individual atoms, but not in three dimensions: it only images the top of atoms). This goal of individual-atom resolution with electron tomography is a great promise but also a great challenge, as it must overcome complications due to electron scattering properties, including multiple scattering, and the interference of the support of the sample.

Challenges of nanomaterials vs. surfaces

Let us compare the challenges of studying the structure of nanomaterials to the more familiar task of determining surface structures.

First, with the various particle-based techniques developed for surfaces (such as LEED and PED), we need vacuum. It is certainly possible to place some nanostructures in vacuum, namely those with free external surfaces. But this prevents us from easily studying the often more important external solid/liquid or internal solid/solid interfaces, not to speak of interfaces with soft matter. With photon-based techniques (such as XRD and XAFS), the challenge is to obtain enough sensitivity to the interfaces of interest, against a background of "bulk" material: for example, even in cylindrical nanorods of radius ~1.5 nm, the surface atoms only comprise about 1% of the total number of atoms, and therefore only about 1% of the measured signal. The interface sensitivity can be enhanced if foreign atoms reside at such interfaces and if only those foreign atoms are detected, as may be possible with XAFS, for example.

Another important consideration is the degree of order in the samples. Most surfaces for which we know the atomic-scale structure have a high degree of order, with crystallinity at least in two dimensions. With nanostructures, the degree of order decreases, of necessity. And the less order is present, the more complex is the structure and the more difficult is its structure determination. This is particularly true of soft matter, which orders less easily than atoms or small molecules.

In nanostructures, one may often expect multiple phases to coexist, for example due to segregation or growth history: the more phases are present, the more difficult it will be to distinguish them. In some instances, distinction by spectroscopic chemical resolution may be possible, as in XAFS. In others, distinction through different diffraction patterns may be possible.

A further complication with nanostructures is the possibility of multiple orientations of individual nanoparticles; they may not have a substrate or template that keeps all particles aligned, as a surface provides. Multiple orientations can angle-average the signal and considerably complicate its analysis. In some cases, distinct diffraction patterns due to the different orientations may be used to separate differently oriented particles.

Most crystalline nanostructures exhibit multiple crystallographic facets, due to termination of the bulk crystal lattice along equivalent or inequivalent crystallographic planes. Inequivalent facets often possess different properties, such as different chemistry. It then becomes desirable to separate the signal measured from different facet orientations. With some diffraction techniques, this may be done through distinct diffraction patterns; otherwise, some sort of deconvolution may be necessary to counter the averaging that takes place.

To study surfaces with photons, one may exploit the freedom to orient the light polarization into different directions: for example, with XAFS, one may orient the light polarization more or less perpendicular and parallel to a given surface. This allows extracting additional directional information about the surface structure. However, with nanostructures that exhibit various orientations, the signal is averaged over those orientations, making it more difficult to extract directional structure information such as molecular orientations or bond angles. And even with nanoparticles that have common orientations, equivalent facets may have different orientations, averaging again over several directions.

In view of all the potential complications listed above, it may become necessary to "divide and conquer", namely to separate the problem into simpler model systems and then recombine the results into the more complex and more complete nanostructure. For example, with samples that expose inequivalent crystalline facets, it may be necessary to fall back on more traditional extended surfaces with single crystalline orientations. In other words, the conventional surface of surface science will likely remain a useful model system to study components of complex nanostructures.

In any event, it is useful to remember that, even with well-defined solid/vacuum surfaces, the results are often controversial and the analyses very time-consuming. There is no reason to believe that the study of nanoparticles will become easier or quicker; in fact, quite the opposite is far more likely, for all the reasons given above!

Conclusions

Our informal discussion of the structural determination of nanostructures leads to several conclusions.

First, there are many shapes and types of nanostructures: therefore one must expect a rich variety of answers, but also a corresponding amount of controversy and confusion.

Only relatively few surface structures and even fewer interface structures are known today, all of which are two-dimensionally extended surfaces or interfaces. There is a need to determine many more such structures, particularly in the case of interfaces, to serve as building blocks in the study of nanostructures.

Many microscopies are currently available to image surfaces and interfaces, with a wide variety of operating conditions: their spatial resolution ranges around 10 to 50 nm, with 0.1 nm attainable with a few techniques. There is a promise, or at least hope, of full 3D atomic resolution, especially with electron tomography (which, however, will require vacuum conditions).

The structural complexity of interesting nanostructures will likely require that we "divide and conquer" the problems, by falling back in part of traditional surface and interface approaches.

Finally, the role of theoretical modeling is likely to grow significantly. This is due in part to the increasing power of computers and improving theoretical techniques. It is also due to the growing difficulty of studying nanostructures experimentally, compared to the possibility of predicting and exploring alternatives computationally.

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